

## COMPARISON OF LOW-SEVERITY COAL PRETREATMENTS FOR SUBSEQUENT CATALYTIC LIQUEFACTION

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### ABSTRACT

Coal can be effectively solubilized by treatment with carbon monoxide reductant in an aqueous solvent (COsteam process). In recent work with U.S. and Australian low-rank coals, sodium aluminate was demonstrated to improve the conversions in the CO/H<sub>2</sub>O system and in water/hydrogen donor solvent mixtures. In this paper, the catalytic hydrotreatment of the solubilized low-severity products from sodium aluminate-catalyzed and uncatalyzed CO/H<sub>2</sub>O reactions of a Wyodak subbituminous coal are compared. Catalytic hydrogenations of the THF-soluble fractions obtained from the two low-severity products were performed with a conventional cobalt-molybdenum catalyst as well as two clay-supported iron catalysts at 425°C for 3 hours in the presence of 1000-psi (cold) H<sub>2</sub>O pressure. Liquefaction with the cobalt-molybdenum catalyst gave 68% conversion to heptane solubles for both the sodium aluminate and the uncatalyzed low-severity reaction intermediates. In contrast, the supported iron catalysts gave much higher conversions for the intermediate from the sodium aluminate-catalyzed reaction compared to those from the uncatalyzed reaction. These results have important implications for multistage liquefaction processing schemes.

Keywords: liquefaction catalysts, coal solubilization catalysts

### INTRODUCTION

Carbon monoxide and water have been utilized in the liquefaction of coal since 1921, when Fischer and Schrader demonstrated the effectiveness of this process (1). Improvements in the COsteam process have increased conversions to soluble products, but extensive depolymerization and hydrogenation of the coal macromolecules require further catalytic hydrotreatment of the COsteam product. The goal of the University of North Dakota Energy & Environmental Research Center (EERC) coal science group is the development of new homogeneous catalysts for the CO reaction. These catalysts are expected to aid in solubilization and preliminary reduction of low-rank coals to a high-quality intermediate product that can be easily catalytically converted to distillate fuels with low heteroatom content.

Catalysis of the first stage of coal liquefaction involves improving the rates of bond cleavage reactions leading to improved solubility and of preliminary reduction reactions so that oils and asphaltenes are produced without extensive retrogressive reactions. The catalysts should be able to interact effectively with the colloidal coal matter, to generate soluble products at moderate temperature. Thus various inexpensive and disposable inorganic agents that are soluble in the reaction vehicle or solvent are being investigated. Sodium aluminate catalyzed the solubilization of Australian coals in the CO/H<sub>2</sub>O system and in water/hydrogen donor solvent mixtures (2, 3). Previous work at the EERC demonstrated that aqueous sodium aluminate was also effective for Wyodak subbituminous coal (4). High conversions comparable to those obtained with hydrogen donor solvents and hydrogen sulfide

were obtained. This paper compares the suitability of the intermediates from catalyzed and uncatalyzed  $\text{CO}/\text{H}_2\text{O}$  reactions as a feed for catalytic hydrogenation.

## EXPERIMENTAL

### Catalyst Preparation

An Amocat-1A cobalt-molybdenum catalyst was presulfided by heating with a small amount of sulfur and 1000 psi of hydrogen in a 15-mL rocking microreactor heated at 350°C for 3 hours. The clay-supported iron catalysts were obtained from Universal Fuel Development Associates, Inc. and were in situ sulfided by adding a small amount of elemental sulfur with the catalyst prior to hydrotreating.

### Coal Solubilization

A slurry consisting of 5.0 g of coal (as-received Wyodak-Clovis Point), 2.5 mmole of  $\text{NaAlO}_2$  (if desired) dissolved in 3.0 g of water and 5.0 g of tetralin (solvent) was placed in a 70-mL Parr reactor. The reactor was evacuated and charged with 1000 psi (initial) of carbon monoxide gas. The reactor was heated to 400°C in a rocking autoclave (initial heatup time = 11 minutes) and left at this temperature for 30 minutes. The reactor was cooled to room temperature, and the gases were removed. The products were distilled to remove water. The remaining slurry was extracted with THF. The THF-insoluble product was dried under vacuum and weighed. The percent conversion was calculated on the basis of the coal (maf) that did not appear in the THF-insoluble fraction. The extract was evaporated to remove THF. The resulting low-severity products from sodium aluminate-catalyzed (SA-LSW) and uncatalyzed reactions (U-LSW) contained the original tetralin as well as the solubilized coal material. These were stored under nitrogen for further catalytic hydrotreating.

The composition of THF-soluble products was determined by adding an aliquot of this product to a large excess of heptane with vigorous stirring. The heptane-insoluble product was separated by centrifugation, washed with heptane, dried in vacuo at 50°C, and weighed. The heptane-soluble product was evaporated to remove heptane and kept for further analyses. The heptane-soluble yield was calculated with the following equation:

$$\% \text{ heptane solubles}^* = \% \text{ conversion} - \% \text{ heptane insolubles}$$

(\* = includes gas and water)

### Catalytic Hydrotreatment of Low-Severity Intermediates

A slurry consisting of 3 g of SA-LSW or U-LSW, 10 wt% of desired catalyst, and 2 wt% of sulfur (if needed) was placed in a 70-mL Parr reactor. The reactor was evacuated and charged with 1000 psi (initial) of hydrogen gas. The reactor was heated to 425°C in a rocking autoclave (initial heatup time = 15 minutes) and left at this temperature for 3 hours. At the end of the reaction, the reactor was cooled to room temperature, and the gases were removed. The product slurry was extracted with THF. The THF-insoluble product was dried under vacuum and weighed. The THF-insoluble fraction was used to determine the amount of coke formed due to retrogressive reactions during hydrotreatment. The extract was diluted to 250 mL with THF. A 4-mL aliquot of the THF-soluble was mixed with 1 mL of solution of internal standard (a mixture of 2,2,4-trimethylpentane and n-octadecane in dichloromethane) and analyzed by gas chromatography (GC). The remaining THF-soluble fraction was evaporated to remove THF, and the dark oil was added to a large excess of heptane and stirred. The heptane-insoluble product was separated by centrifugation, washed with heptane, and dried in vacuo at 50°C. The percent conversion was calculated on the basis of

the heptane-insoluble product that was converted to heptane-soluble product (oils). The conversion and yield data are given in Table 1.

## RESULTS AND DISCUSSION

The advantage of using a solubilization stage in coal processing is that almost all of the inorganic material present in the coal can be eliminated prior to catalytic hydrogenation over a supported catalyst. Thus the calcium deactivation that has seriously affected catalytic liquefaction in the low-rank coals can be avoided. Aqueous solubilization reactions that utilize carbon monoxide as the reductant gas have been extensively investigated in this and other laboratories over many years (5-7). Basic catalysts have been employed to achieve higher conversions. The CO/H<sub>2</sub>O reduction has been shown to be superior to hydrogen for the first stage of liquefaction. A number of candidates for improving the conversion in CO/H<sub>2</sub>O were reported by Jackson and others (2, 3). Aqueous sodium aluminate gave good conversions of brown coal to oils at temperatures of 350° to 400°C. The mechanism for sodium aluminate activation of carbon monoxide to produce an effective reducing intermediate is still under investigation.

Investigations of homogeneous catalysts for coal liquefaction at the EERC (4) verified that sodium aluminate is also effective in improving the CO/H<sub>2</sub>O liquefaction of low-rank western U.S. coals. High conversions to THF solubles were obtained for the Wyodak subbituminous coal (89%). This was substantially higher than that obtained in a similar CO/H<sub>2</sub>O reaction with no added sodium aluminate (78%). Conversion of the Wyodak to THF solubles in a CO/H<sub>2</sub>O liquefaction experiment with sodium hydroxide catalyst was substantially lower (72%).

A mixed solvent containing an organic solvent with lower vapor pressure (tetralin) was also used for the CO/H<sub>2</sub>O reaction. Solubilization reactions of the Wyodak coal were performed in a water-to-tetralin wt/wt ratio of 0.6, both with and without sodium aluminate, at 400°C for 30 minutes with 1000 psi of cold initial CO pressure. Compared with water only, the operating pressure as well as conversions to THF-soluble products was significantly lower for the mixed solvent system. The sodium aluminate-catalyzed reaction gave 79% conversion to THF solubles, whereas the uncatalyzed reaction gave only 63% conversion. The lower yields for the mixed solvent in both catalyzed and uncatalyzed reactions may have resulted from the lower water concentration. The dependence of the conversions on the CO and water partial pressure was previously described (8). It should also be pointed out that the lower fluid density in the mixed solvent reactions may have resulted in a lower conversion. Higher conversions can be obtained by longer reaction times or higher temperatures, but minimal processing severity was desired for generating the intermediates needed for this study.

The yield of heptane solubles from the sodium aluminate-catalyzed reaction (CO/water/tetralin system) was the same (30% heptane solubles) as that obtained in uncatalyzed reactions in the same system (31% heptane solubles). Since the conversions were higher for the sodium aluminate-catalyzed reactions, the heptane-insoluble fraction is larger for the sodium aluminate-catalyzed reactions. Thus the two products do not have the same composition with respect to the solubility fractions.

Development of an economical process for liquefaction of low-rank coals requires an evaluation of the suitability of the soluble COsteam products as a feed for catalytic

hydrogenation. The catalytic hydrogenation is required for depolymerization to a distillable product with higher hydrogen content and low heteroatom content. The evaluation of product quality was determined by carrying out hydrogenations with both a conventional supported cobalt-molybdenum catalyst as well as two dispersed iron sulfide catalysts. In these tests, the THF-soluble low-severity products from the sodium aluminate-catalyzed (SA-LSW) and the uncatalyzed CO/H<sub>2</sub>O reactions (U-LSW) were catalytically hydrotreated with 10 wt% of the catalyst at 425°C for 3 hours in hydrogen (1000 psi cold). Since the compositions of the U-LSW and SA-LSW were not identical, the percent conversion was measured as the percentage of heptane insolubles converted to heptane solubles in the hydrogenation of each intermediate with each catalyst. The conversion data and product yields are given in Table 1.

The thermal (nuncatalytic) hydrogenation of the SA-LSW product converted 24% of the heptane-insoluble fraction to heptane solubles. Thermal hydrogenation of the U-LSW product gave a similar conversion to heptane solubles (26%).

The supported cobalt-molybdenum catalyst was presulfided in hydrogen sulfide/hydrogen (10% H<sub>2</sub>S). Hydrogenation of the SA-LSW with the presulfided cobalt-molybdenum catalyst resulted in a high conversion (68%) of the heptane-insoluble fraction to heptane solubles. Hydrogenation of the U-LSW with this catalyst also gave a high conversion to heptane solubles (67%).

In contrast to the molybdenum catalyst results described above, the results obtained with sulfided iron catalysts demonstrated significant differences for the hydrogenation of the low-severity products obtained from the sodium aluminate-catalyzed and the uncatalyzed reactions. An iron/alumina-pillared montmorillonite catalyst was sulfided in situ by adding elemental sulfur to the reactants. The hydrogenation of SA-LSW with this catalyst gave a 62% conversion to heptane solubles. A conversion of only 47% was obtained with the U-LSW product. The very large increase in conversion to heptane-solubles in the SA-LSW experiment clearly demonstrates that the use of sodium aluminate catalyst in the CO/water pretreatment solubilization stage had a beneficial effect on the quality of the low-severity product.

This improvement in the hydrotreatability of the low-severity product as a result of sodium aluminate catalysis was further demonstrated by a different sulfided iron catalyst. This catalyst was prepared by the impregnation of triiron complex on an acid-washed montmorillonite. Sulfidation was performed in situ with elemental sulfur, and reaction conditions were the same as before. The reaction with the SA-LSW gave an excellent conversion to heptane solubles (67%), which compared favorably with that produced by the molybdenum catalyst. As in the reactions with the pillared clay-supported iron sulfide catalyst, the reaction of this clay-supported iron catalyst gave a much lower conversion (56%) with the U-LSW.

## CONCLUSIONS

The low-severity products from CO/H<sub>2</sub>O reactions obtained with and without sodium aluminate were compared in hydrogenation tests with three catalysts as well the thermal nuncatalytic reaction. The thermal reaction gave poor conversions to heptane solubles for both low-severity products. A significant difference in the conversions of the two low-severity products to heptane solubles was found for two clay-supported iron catalysts. The sodium

aluminate-catalyzed CO/H<sub>2</sub>O reaction gave a product with much higher potential for hydrotreating than that obtained from the uncatalyzed CO/H<sub>2</sub>O reaction. In contrast, a commercial cobalt-molybdenum catalyst gave about 68% conversion for both low-severity products. Thus the very effective hydrogen-activating molybdenum sulfide catalyst was able to compensate for the lower quality of the uncatalyzed reaction product. If the economics of coal liquefaction and catalyst recovery demand the use of the inexpensive and disposable iron catalysts, the use of sodium aluminate in a pretreatment solubilization step will be very important in increasing the yields obtained in the subsequent catalytic hydrogenation step.

#### ACKNOWLEDGMENTS

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Table 1

Catalytic Hydrotreating of Low-Severity Products  
from CO/H<sub>2</sub>O Liquefaction of Wyodak Coal

Reaction Time = 3 hr, H<sub>2</sub> = 1000 psi (cold),  
Low-Severity Product wt = 3 g, Catalyst wt = 0.3 g

Low-Sev. Product	Catalyst	Sulfur (%)	Temp. (°C)	Heptane Insol.	%-Conv. to Heptane Sol.
U-LSW	---	---	---	0.49	---
U-LSW	None	None	425	0.36	26
U-LSW	APC-Fe <sub>3</sub> <sup>a</sup>	(2)	425	0.26	47
U-LSW	K-10/Fe <sub>3</sub> <sup>b</sup>	(2)	425	0.22	56
U-LSW	Co-Moly	(2)	425	0.16	67
SA-LSW	---	---	---	0.61	---
SA-LSW	None	None	425	0.48	24
SA-LSW	APC-Fe <sub>3</sub> <sup>a</sup>	(2)	425	0.23	62
SA-LSW	K-10/Fe <sub>3</sub> <sup>b</sup>	(2)	425	0.20	68
SA-LSW	Co-Moly	(2)	425	0.20	68

<sup>a</sup> Catalyst washed with ethanol prior to drying and calcination.

<sup>b</sup> Triiron was supported on K-10 in ethanol.

SA-LSW = Sodium aluminate-catalyzed low-severity product.

U-LSW = Uncatalyzed low-severity product.